

INTERSTELLAR MATTER

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ABSTRACT

Physical properties of the interstellar medium are discussed, with particular reference to the spectroscopy and the chemical identification of interstellar dust.

1. INTRODUCTION

The material in the region intervening between the stars comprises a vacuum comparable to 10^{-16} torr, a vacuum that is unattainable in the laboratory. Despite the fact that the density of interstellar matter is exceedingly low, the correspondingly large interstellar volume contains sufficient dust and gas such that its total mass is comparable to the mass associated with that of the stars. Specifically, from the work of Oort¹ and Gliese,² based on dynamic considerations of our galaxy, the density of observable stars is 1.5 n cm^{-3} , the density of observable interstellar gas and dust 2.1 n cm^{-3} ; and, since the total density in the galactic plane in the neighborhood of the sun is 6.1 n cm^{-3} , a density of 2.5 n cm^{-3} is still unaccounted for (where n is the density of hydrogen atoms).

Of all the interstellar matter, by far the most abundant element is neutral hydrogen. However, other atoms as well as molecules have been identified. The basic tool by which astronomers have been able to identify gas atoms and molecules has been emission and absorption spectroscopy. A comparison of interstellar absorption spectra with that obtained in the laboratory results in an unambiguous identification of the chemicals involved. Moreover, the Doppler frequency shift of the lines provides velocity determinations of the gas clouds in the interstellar region.

The spectroscopic technique consists of choosing a distant star for the background radiation and then scanning (as a function of wavelength) this continuum radiation whereby absorption lines appear that characterize the material constituting interstellar medium. Those studies have successfully been applied in the visible region and, during the last 16 years or so, were extended to the microwave region where the hydrogen atom and recently (1963) the OH radical were identified at 21 cm and 18 cm respectively. (See Table 1 for a compilation of identified

interstellar atoms, molecules, and the wavelength involved.) Whereas the line widths of atoms and molecules are exceedingly sharp, allowing for velocity dispersion (Doppler shifts of the order of 0.03\AA), a set of diffuse lines are also observed, characterized by line widths extending from 2\AA to roughly 80\AA . Astronomers believe that these lines arise from absorption within the interstellar grains or dust, although there is one other mechanism³ by which a wide line can be obtained from a gas molecule; namely, predissociation. (See Table 2 for an abbreviated list of suggested hypotheses for the origin of these interstellar lines.) This will be discussed in more detail in Section 3. However, the cosmic abundance of the elements (Table 3) does not correspond to the observed intensities of the interstellar lines. The reason is that most of the elements such as hydrogen, oxygen, and nitrogen have their strongest absorption lines in the inaccessible ultraviolet region. Here lies the crux of our present dilemma: Present-day astronomy is handicapped by the earth's atmosphere which absorbs uv radiation below 3100\AA , as well as regions in the infrared. It is anticipated that a lunar-based observatory or an orbiting astronomical satellite will provide the means for observing interstellar lines in these important wavelength regions. It is a relatively safe statement that a great deal of additional information on the interstellar medium, and particularly interstellar dust, will result as soon as these new techniques become available.

2. INTERSTELLAR MOLECULES

As seen from Table 1, the molecules CH, CH^+ , and CN have been identified optically⁴ as early as 1940. The molecule OH was identified⁵ in 1963 as a result of earlier laboratory precision measurement on OH by Townes⁶ and his group at Columbia University (1959). Such precision laboratory measurements facilitated the formidable astronomical search for these absorption features. We will not dwell on the very exciting recent results of maser-like emission from these OH lines. Instead, we wish

to draw attention to the important role that these molecules play in relation to interstellar dust. This in turn is connected with the overall problem of the origin of the dust as well as the molecules. There obviously has to be a continual formation of these molecules in the interstellar medium since the diatomic molecules are rapidly dissociated by the interstellar radiation field. For example, the mean life of CH against dissociation is 4×10^4 years, which is rather short, astronomically speaking. Of all the theories that have been considered on the formation of these molecules, including radiative association, formation on grains, and formation from polyatomic molecules, it seems that the grains play an important role in all these possible processes. For example, a third body is necessary to take up the excess in kinetic energy, or as a site on which protons or nitrogen atoms can combine with carbon, or possibly as the origin of the molecules themselves due to break up of the hydrocarbon grain structure. The latter hypothesis is favored as a result of the model proposed in Section 3. In any event, the presence of diatomic molecules containing carbon as was suggested by Herbig may be an important clue to the possible identification of interstellar dust. For a more recent discussion on these topics, see Ref. 7.

3. INTERSTELLAR DUST

Astronomers have long been aware of the significant role that the interstellar dust plays in our galaxy. It manifests itself by obscuring the light emanating from stars, by scattering and causing the stars to look redder, and by partial alignment of the dust grains in the intergalactic magnetic field causing some of the scattered starlight to be polarized. It is postulated that the observed diffuse absorption lines are associated with the interstellar grains, since the strength of these diffuse lines can be correlated with the amount of interstellar reddening. A summary of the physical properties of dust is shown in Table 4.

A more complete introduction into the general properties of interstellar dust can be obtained from Refs. 8-14. Studies of the wavelength dependence of reddening and polarization are frequently used in assigning models for the dust. However, the diffuse interstellar lines are by far our best clues for the identity of the major component of the interstellar dust. Theories on the origin of the diffuse interstellar lines are listed, by author, in Table 5. Meanwhile, the number of observed diffuse lines is steadily increasing, largely as a result of Herbig's impressive efforts in searching for such lines (25 to date). A list of 17 of them kindly supplied by Herbig in 1963 is shown in Table 6. An examination of these in terms of wavenumbers showed that some of the lines could be arranged to exhibit differences which were multiples of 228 cm^{-1} . This led to the suggestion that the origin of the lines were related to vibronic transitions.¹⁴ A very thorough search was therefore begun for hydrocarbons or related compounds which would fit the astronomical spectra.

The reason for concentrating on hydrocarbons was based largely on stellar abundances and the existence¹² of molecules such as CH and CN in the interstellar medium, which suggested the possibility that carbon might play an important role. Meanwhile, the graphite hypothesis has received a great deal of attention. However, no absorption lines could be ascribed to graphite or ice-coated graphite particles. It is possible that the proposed hydrocarbons might be associated with graphite, though this need not necessarily be so. In searching for hydrocarbons, attention was given to such systems as the conjugated polyene series and other dyes that absorb in the visible region. An examination of the interstellar lines, however, reveals these additional clues:

- a. A large number of lines appear in the red region of the spectrum.
- b. The strongest of the lines occurs at 4430\AA . The spectra is therefore very similar to that found in porphyrins, a large family of organic compounds whose properties have been extensively studied for many years (but not necessarily at 4°K).

The strongest line at 4430\AA is very suggestive of the Soret band. The chemistry of the porphyrins as well as the spectra are readily seen to have some of the desired properties.

The bands of the porphyrins are very strong, corresponding to singlet $\pi\pi^*$ transitions; furthermore, studies of dichroism have shown that the dipole moments of these transitions lie in the plane of the tetrapyrrole structure. The Soret and long wave bands are interpreted in terms of coupling of the orbital magnetic moments of the excited electron and its unexcited partner. The lowest $\pi\pi^*$ transition involves a change in orbital quantum number from 4 to 5. Among the desirable chemical properties of the porphyrins are the fact that some can be heated to temperatures of the order of 500°C without dissociation. In fact, some porphyrins sublime and recrystallize at these high temperatures. It is, in fact, the stability of the porphyrins and the fact that they are strongly coupled resonant structures which makes their choice for the selection for the interstellar dust candidates attractive, since one can visualize the formation of these porphyrins in an atmosphere of hydrogen, carbon, and nitrogen at temperatures corresponding to the $400 - 500^\circ\text{C}$ or possibly higher. Their survival is favored over the other less stable compounds formed in a random process.

The absorption frequencies are varied by adding various appendages onto the basic skeleton structure of the porphyrin molecule. A systematic search of the appropriate absorption bands for hundreds of possible variations of these porphyrin compounds does indeed give structures whose absorption bands correspond closely to those of the interstellar lines.

3.1 EXPERIMENTAL DATA

A compilation of the main absorption lines of these porphyrin compounds is given by Falk.¹⁵ The lines of chlorophyll c at 4440\AA , 5800\AA and 6280\AA

stand out both as to wavelength and intensity ratios in comparing them with the observed interstellar lines. Note that the absorption lines result from dipole transitions in the plane of the tetrapyrrole "head" of the chlorophyll molecule. A hydrocarbon (phytyl) "tail" attached to the molecule contributes nothing to the visible absorption spectrum. More detailed discussion on the chemistry and structure of these compounds in relation to the interstellar dust will be published elsewhere.

Meanwhile, experimental transmission measurements were undertaken on some of these compounds at low temperatures. Figures 1 and 2 give our preliminary results on chlorophyll a and b taken at 77°K. Note the doublet at 4700Å. In addition to the chlorophyll molecule, other closely structurally related compounds, such as the haem a₂ molecule and cytochrome a, exhibit absorption spectra¹⁶ at about 4430Å, 6280Å, and 4000Å in intensity ratios which approximate the instellar lines.

3.2 THE INTERSTELLAR DUST AND LABORATORY DATA

Figure 3 shows the major interstellar lines; not shown are the fainter and relatively sharper diffuse lines. The lines were divided arbitrarily into two groups, one consisting of the widest diffuse lines (whose width varies from 40 to about 80Å) and the stronger but somewhat narrower lines comprising the well-known 4428Å, 6284Å, and 6613Å lines. This figure contains some new unpublished results that were supplied by G. H. Herbig, particularly the doublet 4726 and 4763Å lines, which originally had been thought to be a single feature at 4760Å. The very wide diffuse lines around 4000Å are so far only tentatively identified as interstellar lines. If correct, their presence would play an important role in the identification of the interstellar dust. The arrows indicating laboratory spectra represent major porphyrin-type molecular components including the porphyrin molecule itself (whose Soret absorption band is centered around 4000Å), the haem-type molecules, and various variations of the chlorophyll molecule—particularly chlorophyll c.

These assignments are as yet preliminary and incomplete. Some of the fainter interstellar lines not shown in Fig. 3 might be assigned vibronic transitions in addition to possible small chemical variations of the basic porphyrin molecule.

4. DISCUSSION: LINE WIDTHS

In addition to matching the wavelengths of the laboratory spectra with the interstellar lines, one very important criteria still has to be met; namely, matching linewidths. Here one finds that linewidths are indeed comparable, provided the porphyrins are situated in appropriate matrices.

Personov¹⁷ has succeeded in obtaining low-temperature spectra of a particular group of porphyrins--the phyhalocyanines-- by embedding them in a matrix of paraffins using the Shpol'skii method.¹⁸ Relatively sharp lines are exhibited using this technique. His paper, incidentally, does indeed point to a vibration frequency of 229 wavenumbers. It should also be mentioned that no one has so far succeeded in embedding chlorophyll or haem molecules in an inert matrix using the Shpol'skii technique. Hence the precision of the matching operation does not quite utilize the high precision with which the interstellar lines are measured. Allowing for the fact that there are intensity variations in the ratios of the interstellar lines, satisfactory agreement can be obtained between both the position of the lines and the laboratory intensity ratios to a first order approximation, as indicated in Fig. 3. Figure 4 shows a schematic diagram of the chlorophyll molecule, indicating the two species a and b.

The difficulties associated with laboratory spectra need some emphasis. The absorption measurements of these porphyrins are sensitive to the solvents, pH concentration, temperature, and the environment in which they exist. Consequently, one could hypothesize that if the porphyrins

constitute the major constituents of the interstellar grains, the environment in which these porphyrins exist can be ascertained by an attempt to match the interstellar lines to $\pm 0.5\text{\AA}$. This is a tall order since if one were to match the size distribution, for instance, of the interstellar grains (10^{-5} cm), then scattering would become a severe experimental problem. Since no "glass" or solution remains liquid at 4°K , it is desirable to use single crystal porphyrin compounds. Unfortunately, these are not commercially available. A large number of porphyrin compounds need to be studied under a variety of conditions before final judgment on unambiguous molecular assignments can be made.

5. PREDICTIONS

If indeed the assignments of porphyrin compounds including chlorophyll-like compounds or haems are correct, then one could predict additional lines in the infrared corresponding to 1610, 1652, 1690, 1730, 2720, and 3360 cm^{-1} . In addition, we know that these compounds fluoresce under appropriate conditions. These fluorescent lines would be polarized and should occur in the region between 6000 and 8000\AA --in particular at 6830, 6930, and 7950\AA . Also, some broad absorption lines which are seen in chlorophyll at about 3900\AA and 4200\AA should be looked for in the diffused interstellar bands. These compounds would also be confirmed if interstellar uv absorption data became available. Once the major component of the interstellar dust is identified, checks on duplicating the wavelength dependence of the extinction curves should be carried out both experimentally and theoretically. Following van de Hulst,¹⁹ the extinction cross section is given for a homogeneous sphere by:

$$Q_{\text{ext}} = X \operatorname{Im} \left\{ -4 \frac{\frac{m^2}{2} - 1}{\frac{m^2}{2} + 2} \right\} + X^3 \operatorname{Im} \left\{ -\frac{4}{15} \left(\frac{\frac{m^2}{2} - 1}{\frac{m^2}{2} + 2} \right)^2 \right. \\ \left. \left(\frac{\frac{m^4}{2} + 27 \frac{m^2}{2} + 38}{2 \cdot \frac{m^2}{2} + 3} \right) \right\} + X^4 \operatorname{Re} \left\{ \frac{8}{3} \left(\frac{\frac{m^2}{2} - 1}{\frac{m^2}{2} + 2} \right)^2 \right\} + \dots \quad (1)$$

where

$$X = 2\pi \alpha/\lambda$$

$$\alpha = \text{radius}$$

$$\lambda = \text{wavelength}$$

$$m = \text{complex refractive index}$$

$$Q_{\text{ext}} = \text{cross section divided by } \pi \alpha^2$$

Similar checks on the wavelength dependence of the polarized scattered light also should be carried out. The aforementioned tests would show whether the scattering media that gives rise to reddening and the grains associated with the diffuse lines are one and the same particles.

6. CONCLUSIONS

A brief introductory survey of the interstellar material was presented. The main emphasis in this paper is on the chemical characterization of the interstellar dust by means of absorption spectroscopy. The porphyrin type molecules seem to hold the best promise of being able to match the observed interstellar diffuse line spectra. Some experimental results taken at 77°K are presented. Although the case for porphyrins has not been proven conclusively, the evidence obtained so far is very suggestive that selected molecules from this generic group make up the major component of the interstellar dust.

Acknowledgements

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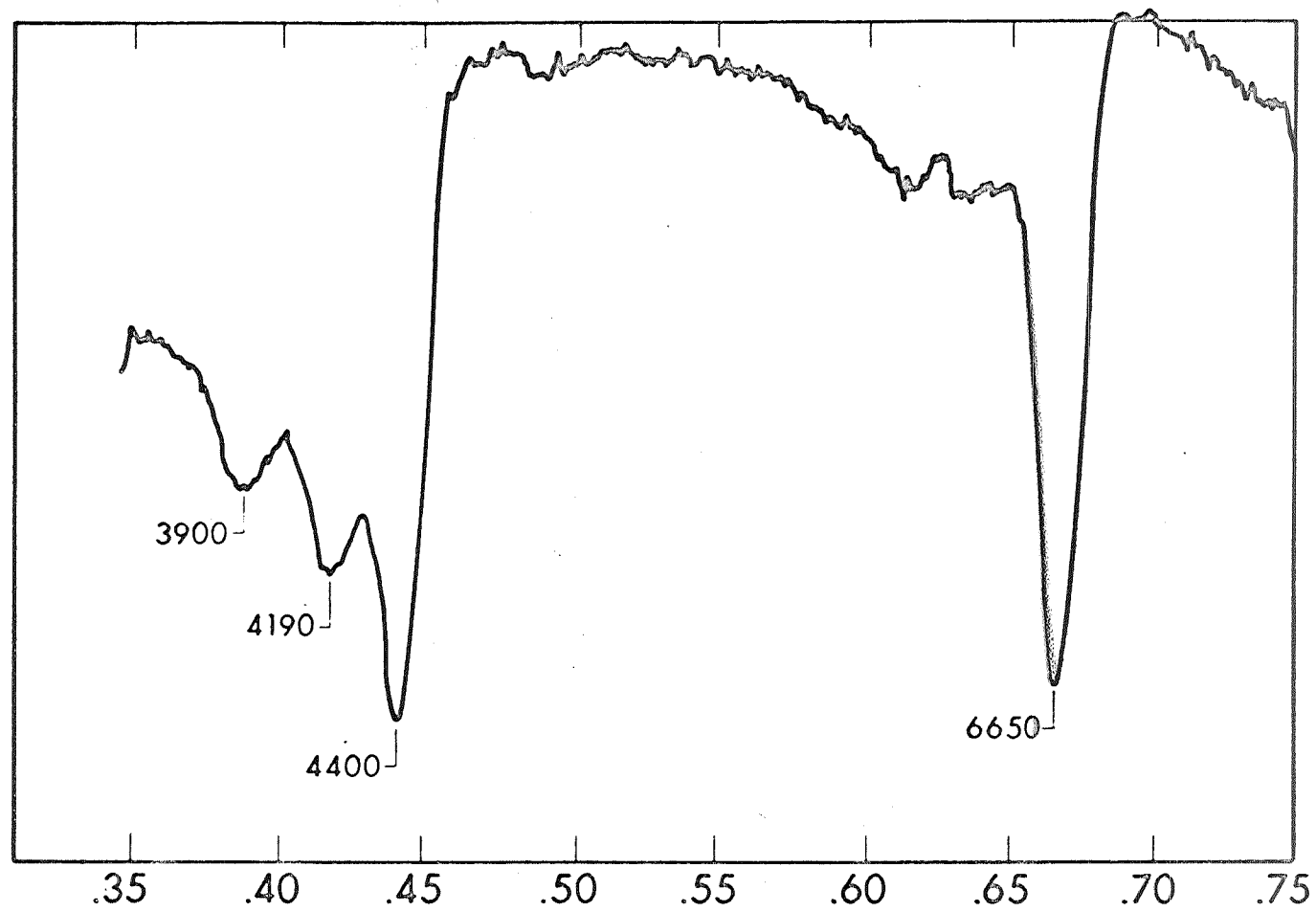


Figure 1

CHLOROPHYLL - a AT 77°K

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TRANSMISSION

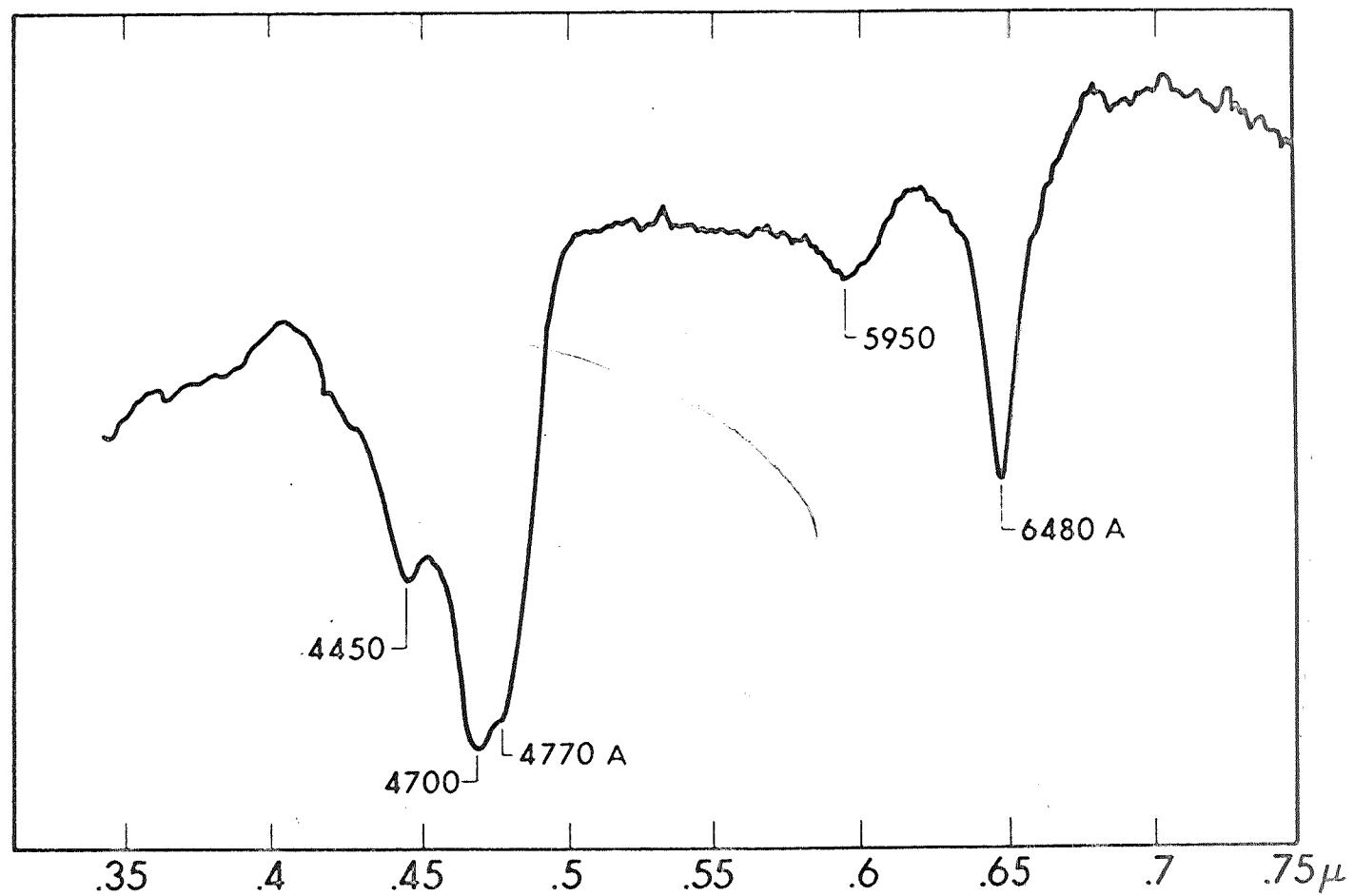


Figure 2

CHLOROPHYLL-b AT 77°K

MAJOR INTERSTELLAR LINES

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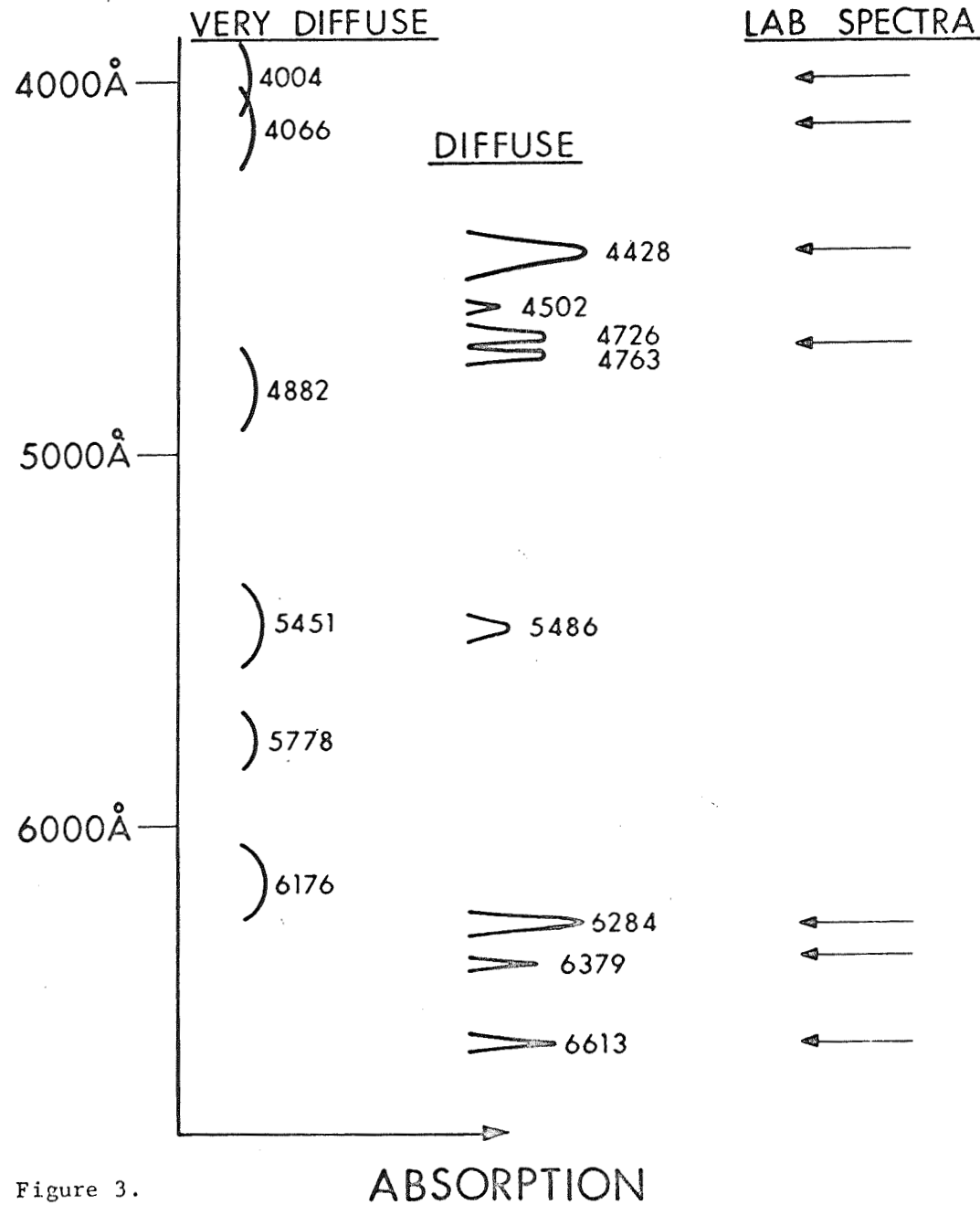


Figure 3.

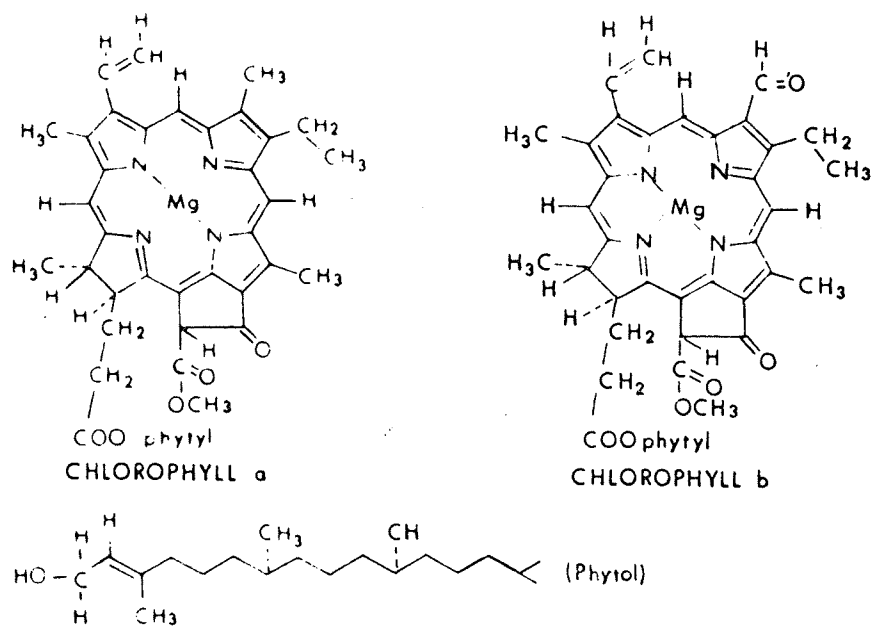


Figure 4. (From "The Chlorophylls" by L. P. Vernon and G. R. Seely)

TABLE 1
INTERSTELLAR LINES

H I Regions				H II Regions	
Atomic Absorption Lines		Molecular Absorption Lines		Emission Lines	
Atom	λ	Molecule	λ	Atom	λ
	A		A		A
Na I	3302.4	CH	3878.8	H	4340.5
Na I	3303.0	CH	3886.4	H	4861.3
Na I	5890.0	CH	3890.2	H	6562.8
Na I	5895.9	CH	4300.3	O II	3726.1
K I	7664.9	CN	3874.0	O II	3728.9
K I	7699.0	CN	3874.6	O III	4958.9
Ca I	4226.7	CN	3875.8	O III	5006.8
Ca II	3933.7	CH ⁺ ?	3580	N II	6548.1
Ca II	3968.5	CH ⁺	3745.3	N II	6583.6
Ti II	3073.0	CH ⁺	3957.7		
Ti II	3229.2	CH ⁺	4232.6		
Ti II	3242.0				
Ti II	3383.8	OH	18 cm		
Fe I	3720.0				
Fe I	3859.0				
H	21 cm				

TABLE 2
HYPOTHESIZED ORIGIN OF INTERSTELLAR LINES

Scheme	Remarks	Ref.
1. (a) Impurities Imbedded in Matrices	Line Width Matrix Shifts }	H. P. Broida R. Wilson
(b) F-Centers	Line width problem	F. M. Johnson
2. Selected Molecules e.g., liq O ₂	Negative Coincidences	A. McKellar
3. Particle Size Dependent Models	No discrete lines Dilemma	A. Unsold J. R. Platt
4. Ice and/or Graphite	No coincidences	
5. Predissociated Bands of Triatomic Free Radicals	No coincidences Lifetime problem	G. Herzberg
6. Specific H-C-N Ring Compounds	Coincidences	F. M. Johnson

TABLE 3
COSMIC ABUNDANCE OF ELEMENTS
(Log Scale)

H	11.9
He	10.9
C	8.2
N	8.4
O	8.7
Na	6.4
Mg	7.5
K	5.4
Ca	6.3
Fe	7.7
Ho	1.4

(Data from Allen)

TABLE 4
PROPERTIES OF INTERSTELLAR GRAINS

Mean Radius of Grain = 3×10^{-5} cm
Mass of Grain = 10^{-13} gram
Mean Density of Grains in Space Near Galactic Plane = 1.4×10^{-26} g cm ⁻³
Mean No. of Grains per Unit Vol. = 2×10^{-13} cm ⁻³
Temperature of Grain 20°K
Asymmetric in Shape and Paramagnetic
(Data from C. W. Allen "Astrophysical Quantities," 1955)